TITLE OF THE INVENTION

MULTI-ELEMENT POLYCRYSTAL FOR SOLAR CELLS AND METHOD OF
MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a polycrystal for
use in a solar cell, formed of a plurality of elements
such as SiGe or InGaAs, and a method of manufacturing
the same.

2. Description of the Related Art

As a method for manufacturing a polycrystal for
use in a practical solar cell at low cost, a cast
method (a kind of solidification method) is known.
Although an Si polycrystal can be formed at low cost
by the cast method, the Si polycrystal cannot absorb
sunlight in a long-wavelength range of the solar
spectrum. Due to this, the light conversion efficiency
of the Si polycrystal is low. On the other hand, as
a high efficiency solar cell, a tandem-form solar cell
is known. The tandem-form solar cell has a hetero-
structure having a thin-film compound-semiconductor
stacked on a Ge or Si. However, the tandem-form solar
cell has a problem in cost. Since it is formed by
epitaxial growth, the cost is high.

As described above, a polycrystal for a solar cell
providing high light-absorption efficiency at low cost
has not yet been obtained. In fact, an appropriate

polycrystal presently developed is chosen depending
upon the use of the solar cell and put in use at
present. However, recently, to use sunlight as a clean
energy source more and more, the technique for
developing a solar cell having a high conversion
efficiency at low cost has been strongly desired.

BRIEF SUMMARY OF THE INVENTION

An object of the present invention is to provide
a polycrystal for a solar cell capable of efficiently
absorbing sunlight at low cost, a method of forming
the polycrystal, and a solar cell obtained by this
method.

To attain the object, the present invention has
the following features.

1. A multi-element polycrystal, which is a mixed
crystal essentially formed of elements A and B having
different absorption wavelength ranges and having
an average composition represented by $A_{1-X}B_X$, in which

the element B absorbs light over a longer range of
wavelength from a shorter to longer wavelength range
than the element A;

each of the crystal grains of the mixed crystal
has a crystallographic texture composed of a plurality
of discrete regions dispersed in a matrix thereof; and

the average composition of the matrix is
represented by $A_{1-x1}B_{x1}$ and the average composition of
the discrete regions is represented by $A_{1-x2}B_{x2}$ where

$X1 < X < X2$.

2. The multi-element polycrystal according to item 1, in which the $A_{1-x}B_x$ is $Si_{1-x}Ge_x$.

3. The multi-element polycrystal according to item 2, in which the X satisfies the relationship: $X \leqq 0.1$.

4. The multi-element polycrystal according to item 2, in which the crystal grains each have a columnar shape, and the discrete regions are three-dimensionally dispersed in the matrix having strain.

5. The multi-element polycrystal according to item 1, which is used in a solar cell.

6. A multi-element polycrystal, which is a mixed crystal essentially formed of elements C, D, and E having different absorption wavelength ranges and having an average composition represented by $C_{1-x}D_xE$,

in which

each of the crystal grains of the mixed crystal has a crystallographic texture having a plurality of discrete regions dispersed in a matrix thereof; and

the average composition of the matrix is represented by $C_{1-x1}D_{x1}E$ and the average composition of the discrete regions is represented by $C_{1-x2}D_{x2}E$, where $X1 < X < X2$

7. The multi-element polycrystal according to item 6, wherein the $C_{1-x}D_xE$ is $Ga_{1-x}In_xAs$.

8. The multi-element polycrystal according to item 6, which is used in a solar cell.

9. A method of manufacturing a multi-element
polycrystal having polycrystalline grains each being
formed of a crystallographic texture having discrete
regions dispersed in a matrix, comprising the steps of:

5   preparing a melt containing multi elements; and

            cooling the melt while controlling a cooling rate
and/or a composition of the melt to obtain a multi-
element polycrystal.

            10. The method according to item 9, in which the

10   melt has a composition for a mixed crystal represented
by $A_{1-x}B_x$; the element B absorbs light over a longer
range of wavelength from a shorter to longer wavelength
range than the element A; each of the polycrystal
grains manufactured has a crystallographic texture in

15   which a plurality of discrete regions having an average
composition represented by $A_{1-x2}B_{x2}$ are dispersed in
a matrix thereof having an average composition
represented by $A_{1-x}B_x$ where X1 < X < X2.

            11. The method according to item 10, in which the

20   element A is Si and the element B is Ge.

            12. The method according to item 10, in which the
X satisfies the relationship: $X \leqq 0.1$.

            13. The method according to item 9, in which

            the melt has components of a mixed crystal

25   represented by $C_{1-x}D_xE$,

            each of the polycrystal grains manufactured has
a plurality of discrete regions dispersed in a matrix

thereof; and

the average composition of the matrix is represented by $C_{1-x1}D_{x1}E$ and the average composition of the discrete regions is represented by $C_{1-x2}D_{x2}E$, where X1 < X < X2.

14. The method according to item 9, wherein the elements C, D and E are respectively Ga, In and As.

15. A method of manufacturing a solar cell by using a multi-element polycrystal manufactured by the method according to item 9.

In the present invention, an average Ge concentration in the SiGe polycrystal is preferably 5 atomic % or less; however, the Ge concentration of the Ge-rich region is preferably 50 atomic % or more.

The present invention is summarized as follows.

The light conversion efficiency of a solar cell can be increased if the solar cell can absorb light over a long range of wavelength, which is the same wavelength range as a solar spectrum has, and convert it to electric energy.

However, an Si polycrystal has a problem in that it absorbs light of a short wavelength and does not absorb that of a long wavelength. Therefore, a solar cell using the Si polycrystal has a low light-conversion efficiency.

In contrast, Ge can absorb light of a long wavelength range. Therefore, if Si is used in

combination with Ge, in other words, if an SiGe
polycrystal is used, it is possible to absorb light
over a long range of wavelength, which has the same
wavelength as a solar light, and convert it to electric

5   energy.   To attain this, it has been considered
that the Ge content of an SiGe polycrystal must be
increased.

However, large content of Ge in the SiGe
polycrystal produces problems: the (short circuit)

10   current density does not increase so much and the
open circuit voltage significantly decreases.   Such
drawbacks of Ge cancel out the advantages of an SiGe
crystal of absorbing light over a long wavelength
range.   This dilemma has not hitherto been overcome.

15   The present invention is characterized in that the
light absorption range by a polycrystal can be extended
to a longer wavelength range by dispersing Ge-rich
regions in the matrix of the polycrystal even though
the entire content of Ge is not increased.   Since

20   the entire Ge content is not increased, the SiGe
polycrystal of the present invention has overcome
the problems: little increase of the current density
and significant decrease in open circuit voltage

As described, the technique of the present

25   invention that a plurality of discrete regions are
dispersed in a matrix may be applied to a process for
forming other multi-element polycrystals to be used in

solar cells, other than an SiGe system. For example,
in the case of an InGaAs system, the object of the
present invention is attained by dispersing a plurality
of In-rich regions in an In-rich matrix rich of each

5   crystal grain thereof.

   According to the present invention, it is possible
to form, for example, a SiGe polycrystal composed of
crystal grains each having a crystallographic texture
in which Ge-rich discrete regions are dispersed in the

10   Si-rich matrix, by controlling cooling conditions, such
as a cooling rate and a super cooling rate, and a melt
composition by use of a method for growing a crystal
from a melt. The crystallographic texture is capable
of absorbing solar light very efficiency and has

15   light-sensitive elements desirably dispersed therein.
According to the present invention, such light
sensitive element regions are successfully dispersed
in the matrix by a practical and simple method, such as
a cast method, thereby manufacturing a polycrystal for

20   a high-efficient solar cell and a solar cell employing
the polycrystal. This method is very practical method
for manufacturing a multi-element polycrystal having
a structure for absorbing light with a high efficiency,
without using a complicated structure such as a tandem

25   structure; and can be applied to manufacturing a multi-
element crystal such as InGaAs.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic view of an SiGe polycrystal grain (SiGe bulk) in which numerous discrete regions are dispersed in the matrix thereof;

5   FIG. 2 is schematic illustrations (A) to (D) showing a crystal grain of a multi-element SiGe polycrystal having discrete regions microscopically dispersed in the matrix, Si/SiGe type-II band alignment, and band gap of SiGe;

10   FIG. 3 is a graph showing the Ge contents of individual sampling points within a crystal grain with respect to the solar cell SiGe bulk polycrystal of the present invention and a conventional SiGe bulk polycrystal (described in Document 1);

15   FIG. 4 is graphs (A) to (D) showing the dependency of solar-cell characteristics upon Ge content with respect to the solar cell of the present invention and conventional ones described in Documents 1 and 2;

FIG. 5 is graphs (A) and (B) showing the
20   performance of a solar cell using an Si bulk polycrystal;

FIG. 6 is graphs (A) and (B) showing the performance of a solar cell using an SiGe bulk polycrystal of the present invention (an average Ge
25   content: 5%);

FIG. 7 is histograms (A) to (D) showing the frequency microscopic distribution of Si contents of

- 9 -

a SiGe polycrystal grain when the polycrystal grain is formed by cooling at different cooling rates;

FIG. 8 is microphotographs (A) to (D) of SiGe polycrystals grown from a melting solution when the polycrystals are formed at cooling rates employed in (A), (B), (C) and (D) of FIG. 7, respectively;

FIG. 9 is a graph showing the relationship between the short-circuit current of a solar cell and the wavelength of the absorbed light with respect to an SiGe polycrystalline solar cell of the present invention having a Si-content frequency distribution shown in (B) of FIG. 7 in comparison with an $Si_{0.5}Ge_{0.5}$ solar cell uniformly formed;

FIG. 10 shows a schematic diagram of an Si/SiGe heterostructure solar cell with a Si thin film epitaxially grown on a multi-element SiGe polycrystal; and

FIG. 11 shows the relationship between internal quantum efficiency and wavelength with respect to a multi-element polycrystalline Si and SiGe.

Description of the Preferred Embodiments

FIG. 1 is a schematic view of an SiGe polycrystal grain (generally having a diameter of several microns to several millimeter) in which numerous discrete regions are dispersed in the matrix thereof. The composition of a crystal grain 10 is represented by $Si_{1-x}Ge_x$. However, the matrix 20 is rich in Si,

whereas the discrete region is rich in Ge.

The reference symbol X in $Si_{1-x}Ge_x$ is preferably
0.1 or less (X≤0.1). Furthermore, each crystal grain
desirably has a columnar structure and preferably has
a high-purity, few defects and an electrically inactive
interface. The Ge-rich discrete regions 30 each have
a planar structure are three-dimensionally dispersed in
a crystal grain. FIG. 2(A) shows a solar cell formed
of the polycrystal thus constructed. This figure shows
a schematic illustration of an Si/SiGe heterostructure
solar cell with Si thin film 40 epitaxially grown on
a multi-element polycrystalline SiGe.

The solar cell having such a structure may have
the following mechanism.

The SiGe polycrystal has numerous Ge-rich regions
dispersed in the Si-rich matrix. The light-absorption
efficiency of such a SiGe polycrystal in a long-
wavelength region is enhanced by adding a small amount
of Ge in the crystal. The solar cell obtained in this
manner must have a good quality. This is because
carrier paths are produced through Ge-rich regions,
so that carriers (electrons) may be prevented from
recombining to each other in the Ge rich regions.
The Si/SiGe heterostructure has a band structure of
type II (see FIG. 2(B)), so that electrons can easily
move from the SiGe crystal to the Si thin layer through
a hetero-junction (p-n junction). The band-gap voltage

decreases by the strain produced in the Ge-rich

regions. Therefore, a large amount of Ge is not

required to be added to the crystal in order to

improve the light absorption efficiency in the longer

5   wavelength range (see FIG. 2(C)).

Furthermore, in the present invention, when

a value, X, of the formula of a crystal grain is

determined by measuring the composition at any given

point within the crystal grain, it was found that

10   the value X varies in a wide range of 0 to 1. The

measurement results are shown in the graph of FIG. 3

in comparison with that of conventional document 1

(P. Geiger, et al., "multicrystalline SiGe Solar cells

with a Ge content of above 10%", Proceedings of 16th

15   European Photovoltaic Solar Energy Conference, 1-5, May

2000, Glasgow, UK, Edited by H. Scheer et al., JAMES &

JAMES, London, Vol. 1, pp. 150-153). Document 1

describes an SiGe bulk polycrystal for a solar cell

having an average Ge content of 10 atomic %.

20   However, the polycrystal disclosed in Document 1

has a uniform composition. More specifically, in

the SiGe polycrystal disclosed in Document 1, it is

found, from the figure shown in Document 1, that

the microscopic compositions of any given points of

25   a crystal grain vary only within the range of ±2% or

less. Even if any SiGe polycrystal tried to be formed

uniformly, such a variance (±2% or less) in composition

inevitably entails. However, a crystal having such a variance in composition is not equivalent to a crystal grain of the present invention having numerous discrete regions dispersed in the matrix.

5   FIG. 3 is a graph showing the Ge contents of individual sampling points within a crystal grain with respect to the solar cell SiGe bulk polycrystal of the present invention and a conventional one (described in Document 1). As is apparent from FIG. 3, the

10   microscopic Ge contents of the SiGe bulk polycrystal for a solar cell according to the present invention varies from site to site in a broader concentration range than that of Document 1. It is therefore found that the composition of the SiGe bulk polycrystal of

15   Document 1 differs from that of the present invention.

The Ge concentrations, volumes, amounts and distribution of the discrete regions within a crystal grain are not simply determined because they differ depending upon the types of raw materials, desired

20   characteristics, and use thereof. Conversely to say, the characteristics of the discrete region can be appropriately determined by those skilled in the art.

The microscopic distribution of the Ge contents of the discrete regions of a polycrystal grain can be

25   designed such that the polycrystal grain can absorb solar light efficiently to convert the solar light into energy as efficient as possible.

The crystal having a microscopically nonuniform composition can be obtained by "controlling the cooling rate of a crystal gain". A preferable cooling rate cannot be simply determined because a desired Ge

5   distribution within a polycrystal differs depending upon the raw materials to be employed, requisite characteristics, and uses thereof.

FIGS. 4(A) to (D) are graphs showing the dependency of solar-cell characteristics upon Ge

10   content with respect to the solar cell of the present invention and conventional ones described in Documents 1 and 2.

FIG. 4(A) shows the dependency of current density upon Ge content; FIG. 4(B), the dependency of open

15   circuit voltage upon Ge content; FIG. 4(D), the dependency of filing factor upon Ge content; and FIG. 4(C), the dependency of external quantum efficiency upon Ge content.

The SiGe polycrystal of the present invention is

20   indicated by a red circle; the SiGe polycrystal of Document 1 (P. Geiger et al.) by a black triangle; and the SiGe polycrystal of Document 2 (M. Isomura et al.) by a blue square.

As is apparent from FIG. 4, the SiGe polycrystals

25   of Documents 1 and 2 contain Ge in an amount of 10 atomic % or more. This is because those skilled in the art believed that a desired conversion efficiency

of a solar cell cannot be improved unless Ge is contained in a large amount before the present application was filed. However, in the solar cell formed of a SiGe bulk polycrystal according to the present invention, a small amount of Ge can be efficiently used by dispersing Ge-rich regions in the matrix. As is apparent from FIG. 4(A), the increase of a short-circuit current density (external quantum efficiency) of the SiGe polycrystals of Document 1 and 2 is low. In addition, the open circuit voltage greatly decreases with an increase of the Ge content. As a result, the conventional solar cells have conversion efficiencies of only about 6%. In contrast, the present invention can provide a conversion rate as large as 17%.

FIGS. 5(A) and 5(B) show the characteristics of a conventional solar cell using Si bulk polycrystal. The Si bulk polycrystal is manufactured in the same conditions as in the SiGe bulk polycrystal shown in FIG. 6.

FIGS. 6(A) and 6(B) are graphs showing the characteristics of a solar cell of the present invention using an SiGe bulk polycrystal, in which Ge-rich regions are dispersed in an Si-rich matrix of a crystal grain, an average Ge content is 5%.

FIGS. 5(A) and 6(A) show the dependency of current density upon voltage and FIGS. 5(B) and 6(B) shows the

dependency of external quantum efficiency upon wavelength.

As is apparent from the comparison between FIGS. 5 and 6, the SiGe bulk polycrystal according to the present invention shown in FIG. 6 can maintain a large short-circuit current density over a wide voltage range and also maintain a large external quantum efficiency over a wide wavelength range. Therefore, it is clear that a solar cell using the SiGe bulk polycrystal having a microscopic dispersion of Ge can has a higher conversion efficiency than that of a Si polycrystal. As is also apparent from Document 1 (P. Geiger et al.), the SiGe bulk polycrystal of the present invention can provide a high conversion efficiency that never been attained by a solar cell using a conventional SiGe polycrystal. There has been no report that shows even the possibility of manufacturing a solar cell having such a high conversion efficiency as in the present invention. This is because those skilled in the art believed that if Ge is contained in a Si polycrystal, the open current voltage greatly decreases. On the contrary to the conventional belief, the data shown in the present specification demonstrates that open current voltage does not decrease until the Ge content reaches about 5 atomic %.

Now, Examples of the present invention will be explained.

First, 1.66 g of Si and 3.71g of Ge are mixed
and melted to prepare a melt of a two- element SiGe
system having a uniform composition. The melt is
cooled at a predetermined cooling rate to obtain
a polycrystal formed of crystal particles each having
a crystallographic texture in which Ge-rich regions are
dispersed in an Si-rich matrix (matrix).

FIGS. 7(A) to (D) are histograms showing the
frequency distribution of the Si contents (shown in
the horizontal axis), which is obtained by measuring a
plurality of sampling points within the crystal surface
for the content of Si. FIG. 7(A) to (D) show the cases
where a melt is cooled at various cooling rates.

The cooling rates of (A) and (B) are 0.5°C/min and
10°C/min, respectively; (C) and (D) are the cases of
air cooling and water cooling, respectively, each case
of which an average content of Si is about 50%.

As is apparent from these graphs, when a melt is
cooled at various cooling rates, crystals having
microscopically different frequency distributions of
Si content can be obtained. For example, a crystal is
solidified to grow while it is cooled at a rate of
10°C/min, the obtained polycrystal having nearly equal
distribution of Si contents can be obtained, as shown
in FIG. 7(B). The polycrystals of FIGS. (A) to (D)
have the structures shown in FIG. 8(A) to (D),
respectively.

FIG. 9 is a graph showing the relationship between the short-circuit current of a solar cell and wavelength with respect to an SiGe polycrystalline solar cell of the present invention and a conventional $Si_{0.5}Ge_{0.5}$ solar cell. To obtain the data of FIG. 9, as a light source having a solar spectrum is used. In the figure, where the note "R=1:1:1:1:1:1:1:1:1:1:1" means that a crystal presumably has microscopic compositions represented by $Si_{1-x}Ge_x$ where X varies by 0.1 from 0 to 1; and the note "d = 2 μm" means the carrier-diffusion distance required in calculation. The SiGe polycrystalline solar cell is formed in accordance with the present invention, that is, the cell has a crystallographic texture having Ge-rich regions scatted in an Si-rich matrix. The $Si_{0.5}Ge_{0.5}$ polycrystalline solar cell, which has a uniform composition, that is, a crystallographic texture having Ge-rich regions are not scatted in an Si-rich matrix, is manufactured by a conventional liquid-phase epitaxy method without controlling the cooling rate.

As is apparent from FIG. 9, the total area (light-trapping area) enclosed by the curve shown by the polycrystalline solar cell according to the present invention is wider than that shown by the conventional $Si_{0.5}Ge_{0.5}$ polycrystal solar cell, even though they have the same Si and Ge contents in average. This means that the solar cell of the present invention

produces a larger amount of current, with the result
that a light-conversion efficiency increases.

In order to further increase the light-conversion
efficiency, a thin film may be deposited on a substrate

5   of SiGe polycrystal according to the present invention
to form a two-layered structure (see FIG. 10). In the
Examples, a SiGe polycrystal is explained. However,
the light-conversion rate can be further improved if
an InAs-GaAs system polycrystal is used. Other that

10   this, a three-element system polycrystal formed of
elements of the III-V group, such as GaSb-GaAs, and
a four-element system polycrystal, such as InAs-GaP and
InAs-GaSb, may be used. In short, any elements may be
used in combination as long as materials have different

15   absorption wavelengths.

As shown in FIG. 9, according to the present
invention, it is possible to obtain a SiGe polycrystal
solar cell capable of providing a short-circuit current
by absorbing the wavelength corresponding to a solar

20   light spectrum. The current thus obtained is larger
than that obtained by a conventional Si polycrystal
solar cell.

Furthermore, as is apparent from the character-
istics of a solar cell shown in FIG. 4(B), open current

25   voltage of the SiGe polycrystal solar cell of the
present invention does not decrease until the Ge
content reaches 5 atomic %. Because of this feature,

the light conversion rate of the solar cell of the present invention becomes larger than a conventional solar cell, a shown in FIG. 4(B).

From FIG. 11, it is clear that the internal quantum efficiency the SiGe polycrystal solar cell of the present invention in the range of a long wavelength range is larger than that of a conventional Si polycrystal solar cell. As a result, the sensitivity of the solar cell to light in a long wavelength range can be increased.

Furthermore, according to the present invention, it is possible to control the sensitivity to the wavelength of the solar light as shown in FIG. 9 by regulating the Si content distribution by varying cooling conditions as shown in FIG. 7. As a result, it is possible to manufacture a solar cell having the most desirable distribution of components and thus absorbing the solar light with high efficiency.